



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (51) International Patent Classification ⁶: G03C 7/06, B41M 3/00, 1/34, G02B 5/20, C09D 11/00, C09B 29/036, 29/46, C08F 8/30 | A1 | (11) International Publication Number: WO 95/34024 (43) International Publication Date: 14 December 1995 (14.12.95) |
| (21) International Application Number: PCT/GB95/01122 (22) International Filing Date: 18 May 1995 (18.05.95) (30) Priority Data: 9411586.2 9 June 1994 (09.06.94) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): CARR, Kathryn [GB/GB]; 143 Hoyles Lane, Cottam, Preston PR4 0NB (GB). HOL- BROOK, Mark [GB/GB]; 2 Spring Close, Ramsbottom, Bury BL0 9SQ (GB). FERGUSON, Ian [GB/GB]; 561 Rochdale Road, Walsden, Todmorden, Lancashire OL14 6SA (GB). (74) Agents: PUGSLEY, Roger, Graham; Zeneca Specialties. Intellectual Property Group, P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB) et al. | | (81) Designated States: AU, BR, CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| (54) Title: PRINTING PROCESS (57) Abstract A process for preparing an optical filter comprising a coloured cross-linked polymeric coating on a transparent substrate, which comprises applying to the substrate, by a printing process, a mixture comprising one or more polymer precursor(s), and one or more dye(s) having one or more heterocyclic NH group(s) or one or more substituent(s) capable of forming a covalent bond with the polymeric precursor, and thereafter curing the mixture. The invention also provides formulations comprising one or more polymer precursors and dyes, optical filters, and a novel dye. | | |

PRINTING PROCESS

This invention relates to processes for printing substrates, to a mixture of polymer precursor and dye, to a process for making optical filters, to optical filters and to novel dyes.

Published European Application No 546,856 proposes a process for making colour filters (for use e.g. in liquid crystal displays) which uses a photosensitive resin resist composition containing a dye which either has a photopolymerisable substituent or has a molecular weight in the range from 500 to 4000. The dye is said to be immobilised in the resin matrix either by its high molecular weight, or by self-polymerisation or by co-polymerisation of the dye with the photosensitive resist resin.

Published European Patent Application No 531,106 proposes colour filters in which the light-filtering substance comprises the result of the reaction of a binder polymer with a reactive dye. The reactive groups in the binder polymer are hydroxy or amino groups, while the reactive dye is of cellulose-reactive type, containing either a vinylsulphone group (or a precursor thereof), or an electrophilic reactive group (e.g. a chlorine atom attached to a triazine ring), or a mixture of these types.

Published European Patent Application No. 564,237 proposes a process of making a colour filter using a photosetting resin precursor and a dyestuff which can uniformly colour the photocured resin.

United States Patent 5,176,971 proposes a method of making a colour filter in which the filter picture elements (red, green and blue) are made of polyimide resin containing a dye.

United States Patent 4,781,444 proposes a method of making a colour filter by electrodeposition of a coloured layer on a substrate. The coloured layer comprises a polymer having a dye chemically bonded to it. The dye used is a cellulose-reactive dye containing for example a vinyl sulphone group or an electrophilic reactive group (e.g. a chlorine atom attached to a triazine ring), as described above for European Patent Application 531,106.

United States Patent 5,231,135 proposes a method of making a coloured polymer coating on a substrate, in which the coloured polymer is prepared by reaction of a colourant of formula $R-[polymeric\ constituent-X]_n$ wherein R is an organic dyestuff radical and X is a reactive moiety (e.g. -OH, -NH₂, or -SH) with a linking agent (e.g. a polyisocyanate or a melamine-formaldehyde resin), which in turn reacts with a polymer having reactive groups and links the colourant with the polymer. In an alternative embodiment, the colourant is reacted directly with the polymer, without a linking agent. The coloured polymers are said to be useful as coatings for automobiles.

According to a first aspect of the present invention, there is provided a process for preparing an optical filter comprising a coloured cross-linked polymeric coating on a transparent substrate, which comprises applying to the substrate, by a printing process, a mixture comprising one or more polymer precursor(s) and one or more dye(s) having one or more heterocyclic NH group(s) or one or more substituent(s) capable of forming a covalent bond with the polymer precursor, and thereafter curing the mixture.

The term heterocyclic NH group means an NH group in which the nitrogen atom forms part of a heterocyclic ring. In many dyes the heterocyclic NH group will itself be capable of forming a covalent bond with the polymer precursor.

The polymer precursor may be any organic monomer, comonomer, polymer or copolymer and mixtures thereof having groups which are capable of reacting directly with the dye(s). Where mixtures of different polymer precursors are used at least one of the polymer precursors is required to be capable of reacting with the dye(s). Examples of polymer precursors include acrylates, methacrylates, acrylamides, methacrylamides, epoxides, esters, urethanes, isocyanates, alcohols, vinylalcohols, imides, amides, phenols, acetates, carbonates and their derivatives, amines, carboxylic acids and orthoformaldehyde condensates, polyacrylic resins, polyvinylalcohol resins, melamine formaldehyde resin condensates, alkyd resins, epoxy resins, polyimides, polyamide resins, phenolic resins, polyester resins, polyvinylacetate, polycarbonate resins, urethane resins and their derivatives and copolymers.

The polymer precursor is preferably selected from acrylamides, epoxides, epoxy resins, acrylamide/epoxy resin systems, melamine formaldehyde resin condensates, polyesters, alkyd resins, hydroxylated or carboxylated acrylics, hydroxylated acrylic-melamine formaldehyde systems and especially from acrylamide/epoxy resin systems and hydroxylated acrylic-melamine formaldehyde systems.

For the purposes of the present specification dye means a compound which absorbs radiation from part of the electromagnetic spectrum and includes compounds which are infra red (IR) or ultraviolet (UV) absorbers which may or may not be coloured and coloured compounds which absorb radiation in the visible part of the electromagnetic spectrum. The dye may be any dye which is capable of covalent bond formation with the polymer precursor; such a dye may be referred to below as a polymer-reactive dye. It is preferably a dye with inherently high light-fastness. The dye may be selected from the monoazo, disazo, azomethine, quinophthalone, cyanine, pyrroline, maleimide, thiophenedioxide, anthraquinone, phthalocyanine, benzofuranone,

benzodifuranone, triphenodioxazine, triphenazonaphthylamine, styryl, dithiene and pyrrole dye classes. Dyes are preferably those which may form covalent bonds with the polymers via a heterocyclic NH group in a heterocyclic part of the dye or via substituent groups selected from

5 -OH; -NHR, -SH or -COOR in which R is -H or alkyl; epoxy; -COalkenyl such as -CO-vinyl and -NHCOalkenyl such as -NHCOvinyl each of which may be attached directly to the dye or via optionally substituted alkyl or aryl groups. The -OH, -NHR and -SH groups are preferably attached to aliphatic carbon atoms (e.g. -CH₂-) to make them more reactive towards

10 polymer precursors. Generally preferred dyes are those which have substituent groups which aid the solubility of the dye(s) in liquid media used in the process or which aid the solubility of the dye(s) in the polymer precursor(s).

A preferred azo dye is a dye of Formula (1):

15



Formula (1)

in which:

20 A is an optionally substituted heterocyclic or carbocyclic group; and

D is an optionally substituted heterocyclic or carbocyclic group or a group of Formula (2):



Formula (2)

25 in which:

E and G each independently is an optionally substituted heterocyclic or carbocyclic group.

The heterocyclic group represented by A, D, E and G may be selected from thienyl, thiazolyl, isothiazolyl, pyrazolyl, benzopyrazolyl, imidazolyl, pyridyl, pyridonyl, thiadiazolyl, furanyl, pyrrolyl, pyridazyl, pyrimidyl, pyrazinyl, benzothiazolyl, benzoisothiazolyl, quinolinyl, isoquinolinyl, indolyl, pyridothiazolyl, pyridoisothiazolyl, triazolyl, pyrrolyl, dioxazolyl, oxazolyl, isooxazolyl, imidazolyl and carbazolyl.

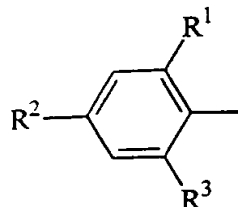
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35 The carbocyclic group represented by A, D, E and G may be phenyl or naphthyl.

A is preferably phenyl, pyrazolyl, triazolyl, pyrrolyl, indolyl or carbazolyl, more preferably phenyl or pyrazolyl.

40

Where A is phenyl it is preferably of Formula (3):



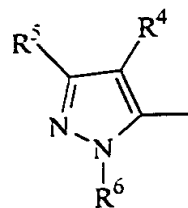
Formula (3)

A preferred sub group of dyes are those of Formula (1) in which A is of Formula (3).

in which:

R^1 , R^2 and R^3 each independently is alkyl, alkoxy each of which may be optionally substituted, -H, -F, -NO₂, -Cl, -Br, -I, -CN, -CN, -SO₂F, -COOR¹⁸, -SO₂R¹⁸, -COR¹⁸, -SO₂NR¹⁸R¹⁹ or -CONR¹⁸R¹⁹ in which R^{18} and R^{19} each independently is alkyl or aryl, each of which may be optionally substituted, or -H.

Where A is pyrazolyl it is preferably of Formula (4):



Formula (4)

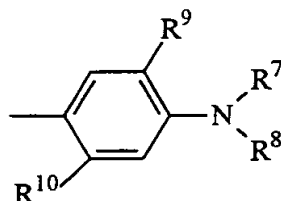
in which:

R^4 is H, -CN, -NO₂, -F, -Cl, -Br, -COR¹⁸, -CONR¹⁸R¹⁹, -SO₂R¹⁸, -CONR¹⁸R¹⁹ or -COOR¹⁸;

R^5 is H, aryl, -CN, -SO₂R¹⁸, alkyl or alkyl substituted by -CN, -CONR¹⁸R¹⁹, -SO₂F or -COOR¹⁸; and

R^6 is H, alkyl, aryl, alkenyl, -SO₂R¹⁸, -COR¹⁸ or alkyl substituted by -CN or -COOR¹⁸.

D is preferably phenyl or pyrazolyl. Where D is phenyl it is preferably a phenyl of Formula (5):



Formula (5)

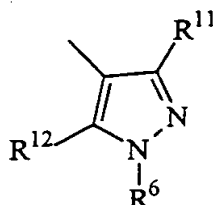
in which:

R^7 and R^8 each independently is -H or alkyl or aryl each of which may be optionally substituted by -OH, -COOH, -COOalkyl, -CN, phenyl, phenoxy, alkoxy, alkyl, -Cl, -Br, alkenyl, alkynyl, -CHF₂, -NH₂, -NHalkyl, -SH, epoxy, -COalkenyl or -NHCOalkenyl.

R^9 is -H, alkyl, alkoxy, -OH, -Cl, -Br, -COOH, -NHCOalkyl, -NO₂ or -COOalkyl; and

R^{10} is -H, -OH, alkyl, -NR¹⁸R¹⁹, -NHCOR¹⁸, -NHSO₂R¹⁸, -NHCONHR¹⁸, -NHCOOR¹⁸ or -NHCOalkenyl.

Where D is pyrazolyl it is preferably of Formula (6):



Formula (6)

in which:

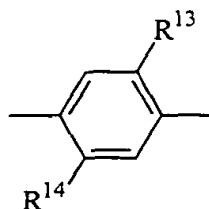
R^{11} is -H, alkyl or aryl;

R^{12} is -NH₂ or -NHalkyl; and

R^6 is as hereinbefore defined.

E is preferably phenyl, thienyl or isothiazolyl, more preferably a phenyl of Formula (7):

5



10

Formula (7)

in which:

R^{13} is -H, -OH, alkoxy, alkoxyalkoxy, -NHCOR¹⁸ or -NHSO₂R¹⁸; and

R^{14} is -H, -NHCOalkyl or -NHCOaryl.

15

G is preferably phenyl or pyrazolyl more preferably a phenyl of Formula (5) or pyrazolyl of Formula (6).

Where a group represented by R, R¹, R², R³, R⁵, R⁶, R⁷, R⁸, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁸ or R¹⁹ is or contains an alkyl or alkoxy group it is preferably a C₁₋₆-alkyl or C₁₋₆-alkoxy group.

20

Where a group represented by R⁵, R⁶, R⁷, R⁸, R¹¹, R¹⁸ or R¹⁹ is or contains an aryl group it is preferably a phenyl or naphthyl group more preferably a phenyl group.

Where a group represented by R⁶, R⁷, R⁸, R¹⁰ is or contains an alkenyl group it is preferably a C₂₋₆-alkenyl more preferably vinyl or allyl.

25

Where a group represented by R⁷ or R⁸ contains an alkynyl group it is preferably C₂₋₆-alkynyl.

The alkyl or alkoxy group or substituents containing alkyl or alkoxy groups represented by any one of R, R¹ to R³ and R⁵ to R¹⁴, R¹⁶, R¹⁸ and R¹⁹ may be straight or branched chain alkyl or alkoxy groups.

30

Where any of the groups represented by A, D, E, G, R¹ to R³, R⁷ and R⁸ is optionally substituted the substituents are preferably selected from -OR¹⁸, -NR¹⁸R¹⁹, -COOR¹⁸, -SO₂R¹⁸, -COR¹⁸, -SO₂NR¹⁸R¹⁹, -CONR¹⁸R¹⁹, -SR¹⁸, -NHCOR¹⁸, -NHSO₂R¹⁸, -NHCOOR¹⁸, C₁₋₆-alkyl and C₁₋₆-alkoxy in which R¹⁸ and R¹⁹ are as hereinbefore defined.

35

R¹, R² and R³ each independently is preferably -F, -Cl, -Br, -CN, -SO₂R¹⁸, -SO₂NHR¹⁸, -NO₂, -CF₃, -COOR¹⁸ or -COR¹⁸ in which R¹⁸ is as hereinbefore defined.

R⁴ is preferably CN, COR¹⁸, CONR¹⁸R¹⁹, COOR¹⁸.

40

R⁵ is preferably phenyl or -CN.

R⁶ is preferably -H.

R⁷ and R⁸ each independently is preferably C₁₋₁₀-alkyl, more preferably C₁₋₈-alkyl or C₁₋₆-alkyl substituted by -OH and

especially alpha-branched C₁₋₈-alkyl or C₁₋₆-alkyl substituted by -OH.

R⁹ is preferably -H, -OCH₃, -NO₂, -CH₃, -COOH, -COOCH₃.

R¹⁰ is preferably -H, -NHCOCH₃, -CH₃, more preferably -NHCOCH₃.

5 R¹¹ is preferably C₁₋₄-alkyl.

R¹² is preferably -NH₂.

R¹³ is preferably -H, C₁₋₆-alkoxy or C₁₋₆-alkoxyC₁₋₆-alkoxy.

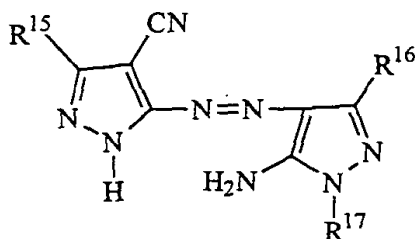
R¹⁴ is preferably -H, -OH, C₁₋₆-alkyl, -NHCophenyl or -NHCOC₁₋₆-alkyl.

10 Further preferred dyes are mono and disazo dyes, especially those having at least one heterocyclic component and particularly those where the heteroatom of the heterocyclic component can react with the polymer precursor to form a covalent bond. Such dyes have the advantage of being stronger, brighter colours with good light and heat fastness

15 properties.

Especially preferred dyes of Formula (1) are of Formula (8):

20



25

Formula (8)

in which:

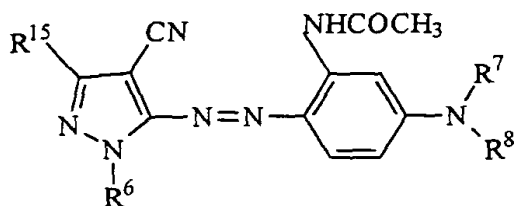
R¹⁵ is phenyl, -CH₂CN or -CN;

30 R¹⁶ is C₁₋₄-alkyl; and

R¹⁷ is -H or phenyl

and Formula (9):

35



40

Formula (9)

in which:

R^6 is -H, C_{1-6} -alkyl or C_{1-6} -alkyl substituted by -CN or -COOC $_{1-6}$ -alkyl;

R^7 and R^8 each independently is C_{1-6} -alkyl, a-branched C_{3-6} -alkyl or C_{1-6} -alkylOH; and

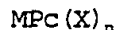
R^{15} is phenyl, -CH₂CN or -CN.

The dyes of Formula (8) form a further feature of the present invention.

A specific example of a dye of Formula (8) is Dye 1 in which R^{15} is -CN, R^{16} is t-butyl and R^{17} is phenyl.

Specific examples of dyes of Formula (9) are Dye 2 in which R^6 is -H, R^7 is ethyl, R^8 is ethyl and R^{15} is -CN and Dye 3 in which R^6 is -H, R^7 is ethyl, R^8 is 1-methylpropyl and R^{15} is phenyl.

A further preferred sub group of dyes are phthalocyanines of the type:



in which

M is H, Si, Ge, metal, oxymetal, hydroxymetal or halometal;

X is or carries a substituent group or atom capable of forming a covalent bond with a polymer precursor;

n is from 1 to 16;

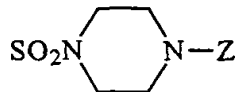
Pc is a phthalocyanine nucleus.

M is preferably H, a transition metal, a halometal, Si or Ge and more preferably H, Ni, Cu, Mn, Fe, Sn, Co, Ti, V, halo Al such as ClAl, haloIn such as ClIn, Si or Ge.

X preferably is a group which carries a heteroatom such as N, O or S, more preferably a substituent group selected from -OH; -NHR, -SR, -COOR, -SO₂R, -SO₂NHR in which R is -H, alkyl, epoxy, -COalkenyl or -NHCOalkenyl or a heteroatom such as N, O or S in a 5-, 6- or 7-membered saturated or unsaturated ring. Each of the substituents or rings containing heteroatoms represented by X may be attached to the phthalocyanine nucleus either directly or via alkyl, aryl, Salkyl, Saryl, Oalkyl, Oaryl, Nalkyl or Naryl groups or any combination thereof.

n is preferably from 1 to 8, more preferably from 1 to 4 and especially 2, 3 or 4.

Preferred phthalocyanines are those having 4 X substituents. Particularly tetrasulphonamidophthalocyanines and especially those in which X is -SO₂NH-R-Z or



in which R is branched or straight chain alkyl, aryl or aralkyl each of

which may be optionally substituted and Z is a group selected from alkyl OH, alkylNH₂, alkylCO₂H preferably alkylOH.

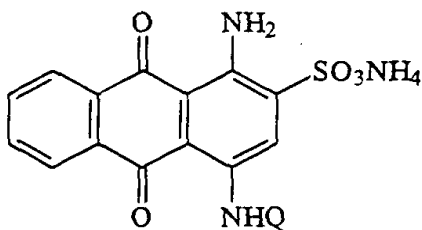
The phthalocyanines are especially useful in coloured films, particularly those prepared by reaction of the phthalocyanine, a thermosetting acrylic polymer precursor and water, which have been applied to glass plates and cured. Such coloured films have excellent heat, light and solvent fastness properties.

A preferred type of dye is a dye in which the substituent capable of forming a covalent bond with the polymer precursor is isolated from the chromophore, for example a dye having an alkylOH substituent. In this type of dye, reaction with the polymer precursor does not cause any appreciable change in colour.

The dyes used in the present invention may be prepared by conventional means. Thus, for example, the monoazo and disazo dyes may be formed by diazotisation of an amine and coupling.

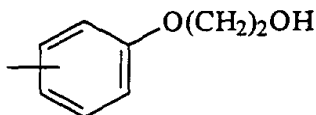
Phthalocyanines of Formula MPc(X)_n may be conveniently prepared by published procedures. For example, heating copper phthalocyanine firstly with chlorosulphonic acid and then with phosphorus pentachloride forms copper phthalocyanine tetra(sulphonylchloride) which may be isolated from the reaction mixture by filtration. The copper phthalocyanine tetra(sulphonylchloride) may be further reacted with an amino compound in a liquid medium such as dioxan to produce a tetra(sulphonamide) derivative.

Preferred anthraquinone dyes include compounds of the Formula (10):



Formula (10)

in which Q is a meta or para linked group of Formula:



The cross-linked polymeric coating may be formed on a substrate to which the coating will bond, adhere, absorb or fuse. Suitable transparent substrates include glass; plastics films and plates such as those of polyvinylalcohol, polyester, polyvinylchloride, polyvinylfluoride, polycarbonate, polystyrene, polyamide or polyimide. A preferred substrate is glass.

The substrates may be pre-treated to improve bonding, adhesion, absorption, fusion or spreading of the cross-linked polymeric coating on the substrate. Suitable pre-treatments include plasma ashing in which the substrate is placed in an oxygen atmosphere and subjected to an electrical discharge or application of an adhesion promoter such as a silane.

In the present process the cross-linking of the polymer precursor(s) may be initiated thermally, chemically or photochemically. Similarly the reaction between the polymer precursor(s) and dye(s) may be initiated thermally, chemically or photochemically. The reaction between polymer precursor(s) and dye(s) may, where they are sufficiently reactive, be initiated simply by mixing the polymer precursor(s) and dye(s) each optionally in a liquid medium and allowing the mixture to air dry.

The mixtures of polymer precursors and specified dyes can also be used to give coloured, transparent films and coatings on substrates in general, including substrates which are not transparent. Accordingly a further feature of the invention provides a process for preparing a transparent, coloured cross-linked polymeric coating on a substrate which comprises applying to the substrate, by a printing process, a mixture comprising one or more polymer precursor(s) and one or more dye(s) having one or more heterocyclic NH group(s) or one or more substituent(s) capable of forming a covalent bond with the polymer precursor, and therefore curing the mixture.

Where the polymer precursor used in processes of the invention is one which is itself capable of cross-linking when cured (e.g. melamine - formaldehyde resin condensate) no additional cross-linking agent need be added to the mixture of dye and polymer precursor. However, where the polymer precursor is one which is not itself capable of extensive cross-linking, it may be desirable to add a cross-linking agent to the mixture of dye and polymer precursor. Thus, for example, in Example 2 below, where acrylamide is used as the polymer precursor, an epoxide is added as a cross-linking agent. The use of cross-linking agents is well known in the polymer art, and the choice of cross-linking agent will be readily made by one skilled in the art.

Where the dye(s) and polymer(s) used in the present process are substantially unreactive at normal temperatures and pressures the

printing process or curing is preferably carried out at a temperature of from 80°C to 250°C, more preferably at from 100°C to 200°C and especially at from 110°C to 180°C.

5 Chemical initiation may be achieved by addition of agents such as epoxides, amines, ammonia, acids, dicyandiamides and acid anhydrides.

10 Photochemical initiation may be achieved by addition of initiators for example azides, ketones such as acetophenone or benzophenone, ketals such as benzyldimethyl ketal, peroxides such as benzoyl peroxide or aryl sulphonium salts such as diphenyl-(4-phenylthio)-phenyl sulphonium tetrafluorophosphate, followed by irradiation with UV or visible light.

15 Thermally initiated cross-linking and reaction is preferred since it has the advantage of simplicity (avoiding the need to add initiators, etc to the mixture) over chemical and photochemical initiation.

20 The mixture of polymer precursor(s) and dye(s) used in the present process may further comprise one or more formulating agents and one or more liquid(s) may be added to the mixture to improve the solubility of dye in the polymer precursor(s) and vice versa, and to improve the flow and handling properties of the mixture. The liquid(s) may be aqueous or organic. The liquid is preferably water, an aromatic hydrocarbon such as toluene or xylene, a ketone such as cyclohexanone, 2-pyrrolidone, N-methylpyrrolidone, methyl ethyl ketone, an ester such
25 as ethyl acetate or ethyl propionate, an alcohol such as methyl, ethanol or isopropanol, glycols such as ethylene glycol, diethyleneglycol, hexylene glycol, glycol ethers such as ethylene glycol monobutylether, ethers such as tetrahydrofuran or mixtures thereof. More preferably the liquid is a ketone such as methyl ethyl ketone or water, or mixtures
30 thereof.

Where a liquid(s) is added to the mixture the printed substrate may be dried by heating or by air drying at ambient temperature to evaporate the liquid before the coating is cured or during curing.

35 The mixture of polymer precursor(s) and dye(s) may further comprise one or more pigments. Such pigments generally do not react with the polymer precursor(s) or the dye(s) and may be used in combination with the dye(s) for shading purposes. Where the dye(s) is not significantly coloured i.e. it is an IR or UV absorber as described
40 above the pigment may be the sole colorant.

In the present processes the printing process may be any printing process such a flexographic, off-set lithographic, gravure, intaglio printing, ink-jet, dye diffusion thermal transfer and screen

printing processes. The printing process is preferably ink-jet printing, especially thermal or piezoelectric ink-jet printing. The principles and procedures for ink jet printing are described in the literature for example in High Technology Applications of Organic Colorants, P. Gregory, Chapter 9 ISBN 0-306-43637-X.

According to a further feature of the present invention there is provided a formulation comprising a mixture comprising one or more polymer precursor(s) and one or more dye(s). The polymer precursor(s) and dye(s) are as hereinbefore defined.

Optical filters, alternatively known as colour filters, are used in liquid crystal displays, for example in small television receivers.

A process for preparing an optical filter according to the present invention may comprise the steps of:

(1) mixing a polymer precursor(s) of for example an acrylic resin, a dye(s) and optionally a dispersant such as an anionic types for example lignosulphonates and other sulphonated aromatic species or non-ionic types for example alkylene oxide adducts in a suitable mixing apparatus such as a three-roller roll mill and mixing in an aqueous or organic solvent or a combination of the two in the mixing apparatus;

(2) adding as appropriate for chemically or photochemically initiated systems either a radical source or a combination of a photopolymerisation initiator and polymer precursor(s) to the resultant preparation for producing a varnish coloured in one of the desired colours such as typically the three primary additive colours of red, green and blue;

(3) forming on the surface of a transparent substrate a multiplicity of discrete filter regions of the varnish distributed in a desired pattern and optically setting the individual filter regions;

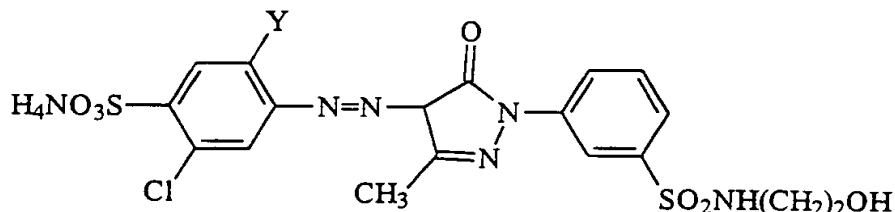
(4) heating the optically set filter regions on the substrate causing reaction of the polymer precursor(s) and dye(s) contained in the filter regions and thereby forming discrete filter elements of a optical filter composition comprising the polymer, dye(s) and optional dispersant.

The discrete coloured filter regions of the optical filter composition may be formed in step (3) by forming a uniformly thick layer of the coloured varnish on the surface of the substrate and subsequently patterning the layer of the coloured varnish into discrete filter regions distributed in a desired pattern while optically setting the individual filter regions. Alternatively, the discrete coloured filter regions may be formed by applying the varnish in a desired pattern onto the surface of the substrate.

The steps (1) to (4) are followed for each of the desired colours to form a multi-colour optical filter structure so that the filter structure finally comprises the transparent substrate and a single layer of differently coloured filter elements arranged in triads or in any desired groups each consisting of a predetermined number of differently coloured filter elements.

Where the process used for applying the polymer precursor/reactive dye mixture to the transparent substrate is ink jet printing, it is possible to achieve printing of all three primary colours (red, green and blue) simultaneously to form triads or any desired groupings of filter elements by using a printing head having appropriately designed outlets for the three coloured polymer precursor/reactive dye mixtures.

Red filter elements prepared according to the invention are usually made by using a mixture of magenta and yellow dye. Specific examples of yellow dyes include those of Formula (8) above in which R^{15} is cyano or cyanomethyl, R^{16} is tert butyl, and R^{17} is phenyl. These dyes are soluble in organic solvents. Examples of water-soluble yellow dyes include those of the following Formula:



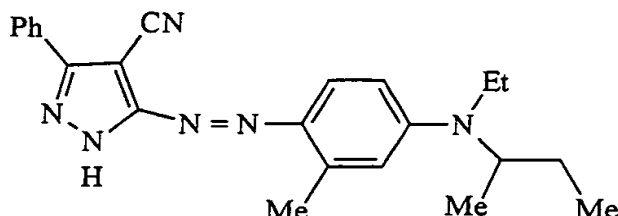
in which Y is Cl or SO_3NH_4 .

Examples of magenta dyes include compounds of Formula (9) above having the substituents shown in the following table :

| R^6 | R^{15} | $-\text{NR}^7\text{R}^8$ |
|-------|-----------------|-------------------------------------|
| H | Ph | $-\text{N}(\text{Et})_2$ |
| H | Ph | $-\text{N}(\text{Et})(2\text{-Bu})$ |
| H | NCCH_3 | $-\text{N}(\text{Et})(2\text{-Bu})$ |

and the compounds of the following Formula:

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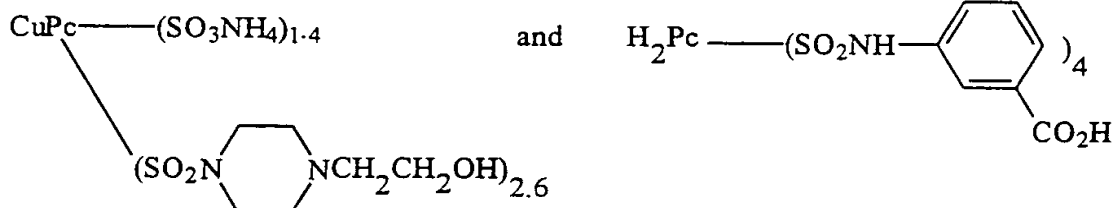


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These compounds are soluble in organic solvents. Me is methyl, Et is ethyl, Bu is butyl and Ph is phenyl.

Green filter elements prepared according to the invention are usually made by using a mixture of cyan and yellow dyes.

Examples of cyan dyes include phthalocyanine dyes having the following formulae :



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These dyes are water-soluble.

Blue filter elements prepared according to the invention are usually made by using a single blue dye. Examples of blue dyes include the phthalocyanines shown above.

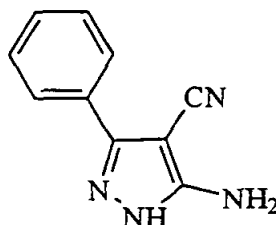
According to a further feature of the present invention, there is provided an optical filter comprising red, green and blue filter elements, and comprising a coloured cross-linked polymeric coating in a transparent substrate, in which at least one of the filter elements comprises a dye covalently linked to the polymer of the polymeric coating as a result of reaction between a heterocyclic NH group in the dye, or a substituent in the dye, and the polymer precursor used to form the polymeric coating.

Usually, at least the red and the green elements of the colour filter will contain a dye covalently bonded to the polymer, while the blue element may contain an anthraquinone dye of the formula above which is not covalently bonded to the polymer.

The polymer precursor(s) and dye(s) are as hereinbefore defined.

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The invention is further illustrated by the following examples:

Example 1Preparation of 2-(4-cyano-3-phenyl-1(H)-pyrazole-2-azo)-5-(N-sec-butyl-N-ethylamino)-acetanilide(i) 5-Amino-4-cyano-3-phenyl-1(H)-pyrazole

1. A solution of triethylamine (98%, 66.66g, 0.71mol) in dry toluene (500ml) was added over 2 hours to a stirred solution of malononitrile (21.78g, 0.07mol) and benzoyl chloride (46.4g, 0.08mol) in dry toluene (300ml) whilst maintaining a temperature of below 35°C. The mixture was stirred for a further 2 hours at room temperature before being allowed to stand overnight. The mixture was filtered to remove the triethylammonium chloride. This was washed with one portion of toluene (200ml). A dark oil settled out in the filtrate which was isolated by decanting off the bulk of the solvent and removing the rest by evaporation under reduced pressure. The viscous oil was acidified with dilute aqueous sulphuric acid (2M, 1l) and the acidic solution was extracted with diethyl ether (4x100ml). The combined extracts were dried over anhydrous magnesium sulphate, filtered and the solvent was evaporated under reduced pressure. The viscous black residue was redissolved in methanol (30ml) and precipitated by pouring into a large volume of cold water. The buff coloured solid was collected by suction filtration and recrystallised from water to yield the required benzoyl malononitrile (13.36g, 24%) as an off white solid.

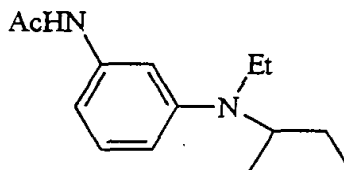
2. Dimethyl sulphate (67.52g, 0.54mol) was added slowly to a stirred solution of benzoyl malononitrile (12.92g, 0.08mol) and sodium bicarbonate (50.65g, 0.60mol) in water (12ml) and 4,4-dioxane (122ml). The temperature was elevated to 80-90°C and maintained for 2 hours. After cooling, the mixture was poured into iced water (1.5l) and the precipitate was collected by suction filtration, washed with water and dried *in vacuo* to afford the methylated product (9.44g, 68%) as an off white solid.

3. The product from the above reaction (9.2g, 0.05mol) was slurried in methylated spirits (40ml). Hydrazine hydrate (100%, 25g, 0.50mol) was added slowly with cooling to maintain the temperature of

the reaction mixture between 25-30°C. When the addition was complete, the temperature was raised to 80-85°C for 1 hour. After cooling, the reaction mixture was poured into iced water (500ml) and the fine, white precipitate was collected by suction filtration, washed and dried in vacuo. This furnished the requisite diazo component (8.34g, 91%) as a white solid.

(ii) 3-(N-sec-Butyl-N-ethylamino)-acetanilide

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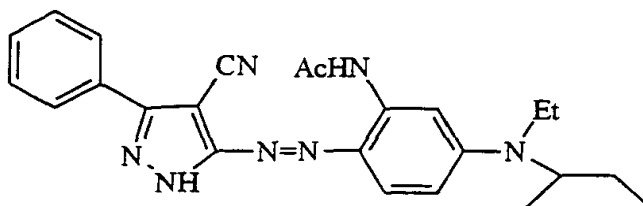


1. A mixture of 3-amino acetanilide (146.7g, 0.45mol), sec-butyl bromide (74g, 0.54mol) and potassium carbonate (68.25g, 0.49mol) in dimethyl formamide (300ml) was stirred at 90°C overnight. After cooling, the mixture was diluted with saturated sodium chloride solution (500ml) and extracted with dichloromethane (200ml). The organic extract was washed with water (2x200ml), dried over anhydrous magnesium sulphate and filtered. Evaporation of the solvent in vacuo gave the N-sec-butyl derivative (34.13g, 37%) as a viscous brown oil which solidified on standing.

2. A mixture of the 3-(N-sec-butylamino)-acetanilide (6.19g, 0.03mol), bromoethane (4.36g, 0.04mol) and calcium carbonate (4g, 0.04mol) in water (80ml) was stirred at 80°C for 16 hours. After cooling to room temperature, the mixture was extracted with dichloromethane (2x150ml). The combined extracts were dried over anhydrous magnesium sulphate and filtered and the solvent was removed in vacuo to afford the product (6.83g, 97%) as a brown oil.

(iii) 2-(4-Cyano-3-phenyl-1(H)-pyrazole-2-azo)-5-(N-sec-butyl-N-ethylamino)-acetanilide

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A solution of sodium nitrite (1.15g, 0.02mol) in water (3.5ml) was added slowly to a stirred ice cold solution of 5-amino-4-cyano-3-phenyl-1(H)-pyrazole (0.73g, 0.004mol) in glacial acetic acid (35ml) and concentrated hydrochloric acid (4.2ml, 0.04mol). The temperature was kept below 5°C during the period of addition and for a further hour afterwards. Excess nitrous acid was destroyed by the addition of a small amount of solid sulphamic acid. The cold diazo solution was added to a solution of 3-(N-sec-butyl-N-ethylamino)-acetanilide (0.92g, 0.004mol) in water (45ml) and concentrated hydrochloric acid (3.5ml) cooled to below 5°C. The mixture was stirred for 1 hour at this temperature before being diluted with water (100ml). Solid sodium acetate was added until the mixture was no longer acid to Congo Red paper. After 1 hour at room temperature, the precipitated solid was collected by suction filtration and washed with water. The damp paste was dissolved in dichloromethane (75ml) and washed with water (3x50ml). The dichloromethane solution was dried over anhydrous magnesium sulphate, filtered and evaporated to dryness *in vacuo*. Dry column chromatography of the crude product furnished the pure monoazo dye (0.4g, 24%) as a dark red solid.

Example 2

Preparation and Use of Inks for Glass Coating

A stock polymer precursor solution can be prepared by mixing the following components: 56.65% by weight SYNOCRYL 836S (an acrylamide available from Cray Valley Products), 8.0% EPIKOTE 1001 X75 (an epoxy available from Shell Chemicals) and 35.35% methyl ethyl ketone (MEK).

Ink samples can be made as follows: A mixture of the stock solution (0.31g), dyestuff (0.05g) and MEK (0.13g) is shaken in a small vial with glass beads until homogeneous.

The resultant ink which contains 10% dyestuff and 25% solid resin can be coated onto a clean glass surface using a suitable wire-wound coating bar to give a wet film thickness of ca. 6mm, eg using a No. 1 K-bar as supplied by RK Print-Coat Instruments Ltd. The coating is dried for 30 minutes at ambient temperature before the resin is fully cured by heating at a temperature of 180°C for 30 minutes.

The cured film is approximately 2mm in thickness and exhibits excellent transparency, adhesion and resistance to strong organic solvents. In addition, heat resistance is excellent (2 hours at 200°C; $DE_{ab} < 5$) as is the photostability (200 hours at 67Klux; $DE_{ab} < 5$).

Example 3

This Example illustrates a typical formulation of polymer-reactive dye and polymer precursor suitable for application to a transparent substrate by ink-jet printing.

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| | <u>Constituent</u> | <u>Percentage by Weight</u> |
|----|--|-----------------------------|
| | Stock polymer precursor (see below) | 50 |
| | Ethylene glycol | 20 |
| 10 | Distilled Water | 24 |
| | Ammonia solution (density 0.880) | 2 |
| | Dye (solid, water soluble) | 4 |

15 The stock polymer precursor is made up of the following constituents :

| | <u>Constituent</u> | <u>Percentage by Weight</u> |
|----|-------------------------------|-----------------------------|
| | CYMEL 327 (90% strength) | 11 |
| | Distilled Water | 18 |
| 20 | 2-Amino-2-methyl-1-propanol | 0.5 |
| | 2-Methyl-2,4-pentane diol | 3 |
| | 2-n-Butoxyethanol | 2 |
| | SURFYNOL 104E | 0.5 |
| | NEOCRYL XK69 (47.5% strength) | 65 |

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Notes

CYMEL 327 is a melamine-formaldehyde condensate included as a cross-linking agent.

The 2-amino-2-methyl-1-propanol is added as a base.

30 The 2-methyl-1-2,4-pentanediol and the 2-n-butoxyethanol are added as coalescents.

SURFYNOL 104E is a surfactant comprising a hydroxyalkyl alkyne.

NEOCRYL XK69 is a styryl-(meth)acrylate co-polymer.

CLAIMS

1. A process for preparing an optical filter comprising a coloured cross-linked polymeric coating on a transparent substrate, which comprises applying to the substrate, by a printing process, a mixture comprising one or more polymer precursor(s), and one or more dye(s) having one or more heterocyclic NH group(s) or one or more substituent(s) capable of forming a covalent bond with the polymeric precursor, and thereafter curing the mixture.

2. A process for preparing a transparent, coloured cross-linked polymeric coating on a substrate which comprises applying to the substrate, by a printing process, a mixture comprising one or more polymer precursor(s) and one or more dye(s) having one or more heterocyclic NH group(s) or one or more substituent(s) capable of forming a covalent bond with the polymer precursor, and therefore curing the mixture.

3. A process according to claim 1 or claim 2, wherein the printing process comprises ink-jet printing.

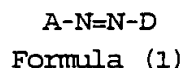
4. A process according to any one of the preceding claims wherein the substrate is glass.

5. A process according to any one of the preceding claims wherein the polymer precursor(s) is/are selected from acrylamides, epoxides, epoxy resins, acrylamide/epoxy resin systems, melamine formaldehyde resin condensates, polyesters, alkyd resins, hydroxylated or carboxylated acrylics and hydroxylated acrylic-melamine formaldehyde systems.

6. A process according to any one of the preceding claims wherein the polymer precursor(s) is/are selected from acrylamide/epoxy resin systems and hydroxylated acrylic-melamine formaldehyde systems.

7. A process according to any one of the preceding claims wherein the dye is selected from the monoazo, disazo, azomethine, quinophthalone, cyanine, pyrroline, maleimide, thiophenedioxide, anthraquinone, phthalocyanine, benzofuranone, benzodifuranone, triphenodioxazine, triphenazonaphthylamine, styryl, dithiene and pyrrole dye classes.

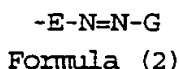
8. A process according to any one of the preceding claims wherein the dye(s) is/are of Formula (1):



in which:

A is an optionally substituted heterocyclic or carbocyclic group; and

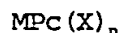
D is an optionally substituted heterocyclic or carbocyclic group or a group of Formula (2):



in which:

E and G each independently is an optionally substituted heterocyclic or carbocyclic group.

9. A process according to any one of claims 1 to 7 in which the dye(s) is/are of the Formula:



in which

M is H, Si, Ge, metal, oxymetal, hydroxymetal or halometal;

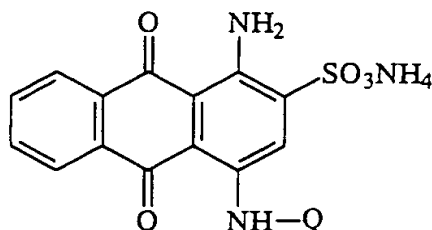
X is or carries a substituent group or atom capable of forming a covalent bond with a polymer precursor;

n is from 1 to 16;

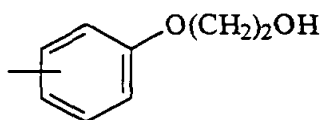
Pc is a phthalocyanine nucleus; and

M is H, a transition metal, a halometal, Si or Ge.

10. A process according to any one of claims 1 to 7 in which the dye has the Formula:



wherein Q is a meta or para linked group of Formula:



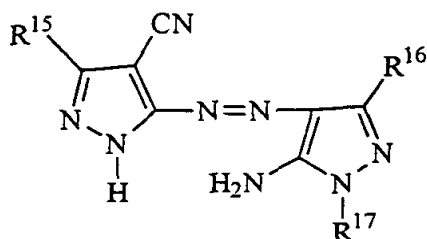
11. A process according to any one of the preceding claims wherein the mixture is cured thermally.

12. A composition comprising one or more polymer precursor(s) and one or more dye(s) in which the polymer precursor is selected from acrylamides, epoxides, epoxy resins, acrylamide/epoxy resin systems, melamine formaldehyde resin condensates, polyesters, alkyd resins, hydroxylated or carboxylated acrylics, hydroxylated acrylic-melamine formaldehyde systems and the dye has one or more substituent(s) capable of forming a covalent bond with the polymer precursor.

13. A formulation according to claim 12 which further comprises a diluent comprising water or an organic liquid or a mixture thereof, and optionally a surfactant.

14. An optical filter, comprising red, green and blue filter elements, and comprising a coloured polymeric coating on a transparent substrate, in which at least one of the filter elements comprises a dye covalently bonded to the polymer of the polymeric coating as a result of reaction between a heterocyclic NH group in the dye, or a substituent in the dye, and the polymer precursor used to form the polymeric coating.

15. A dye of Formula (8):



Formula (8)

in which:

- R^{15} is phenyl, $-CH_2CN$ or $-CN$;
- R^{16} is C_{1-4} -alkyl; and
- R^{17} is $-H$ or phenyl.

16. 2-(4-Cyano-3-Phenyl-1(H)-pyrazole-2-azo)-5-(N-sec-butyl-N-ethylamino)-acetanilide.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G03C7/06 B41M3/00 B41M1/34 G02B5/20 C09D11/00
C09B29/036 C09B29/46 C08F8/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03C B41M G02B C09D C09B G02F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
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| X | US,A,5 231 135 (G.MACHELL ET AL.) 27 July 1993 cited in the application see column 2, line 57 - column 3, line 11 see column 4, line 8 - line 19 see column 4, line 56 - line 66 see claims 1-15; examples 1-13 --- | 12 |
| X | DE,A,35 09 198 (CANON K.K.) 14 November 1985 see claims 1-27; examples 1-16 see page 14, line 12 - page 15, line 16 see page 17, line 13 - page 25, line 3 --- | 14 |
| | --- -/-- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

12 October 1995

Date of mailing of the international search report

20. 10. 95

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | EP,A,0 449 012 (DAI NIPPON INSATSU K.K.) 2 October 1991 see page 2, line 30 - page 3, line 30 see claim 1; figure 1; examples 1-4 --- | 1-14 |
| A | WO,A,85 04679 (BARNES-HIND, INCORPORATED) 24 October 1985 see page 1, line 20 - page 2, line 10 see page 4, line 25 - line 26 see page 6, line 9 - page 8, line 7 see claims 1-18 --- | 1-13 |
| A | EP,A,0 492 444 (EASTMAN KODAK COMPANY) 1 July 1992 see claim 1; examples 1-3; table 1 ----- | 15,16 |

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Information on patent family members

International Application No

PCT/GB 95/01122

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